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吸放氢处理对$La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}B_{0.2}$合金磁热效应的影响*

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摘 要 使用工业纯度原材料制备出$La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}B_{0.2}$合金, 用XRD和VSM分析了合金的析出相、居里温度和磁热性能, 研究了吸氢放氢处理对合金磁热性能的影响。结果表明:退火合金经0.13和0.2 MPa吸氢处理后居里温度分别达到320和321 K, 吸氢压力高的样品放氢困难; 经0.13 MPa吸氢样品在473 K放氢后居里温度降低到室温范围。放氢导致氢化物最大磁熵变降低和相对制冷能力RCP的提高。

关键词 金属材料, 磁性材料, 磁热性能, 放氢, 稳定性, 居里温度

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Influence of Hydrogen Absorption and Desorption on Magnetocaloric Effect of $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}B_{0.2}$ Alloy

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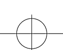
ABSTRACT The $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}B_{0.2}$ alloy was produced by using industrial grade raw materials. The phase constituents and thermal magnetic properties of the alloy were characterized by X-ray diffraction with Cu kα radiation and vibration sample magnetism respectively. The influence of hydrogen absorption pressure on magnetocaloric effect and hydrogen desorption process were investigated. Results show that the annealing treated alloy was subjected to hydrogenation at 0.13 and 0.2 MPa, correspondingly its Curie temperature increased to 320 and 321 K respectively. The taking place of dehydrogenation was much easier for the alloy hydrogenated at lower absorption pressure rather than that at higher pressure. The Curie temperature of the alloy hydrogenated at 0.13 MPa and then dehydrogenated at 473K could lower to room temperature range, correpondingly the maximal magnetic entropy of the hydrides decreased while the relative cooling power were increased.

KEY WORDS metallic materials, magnetic materials, magnetocaloric properties, hydrogen desorption, stability, Curie temperature

开发具有室温大磁热效应的磁性材料是国内外高校和科研机构的研究热点之一[1-4]。尤其是$NaZn_{13}$型晶体结构的$La(Fe, Si)_{13}$基合金, 具有磁热效应大、稀土含量低、无毒性元素和易于合金化制备等特点, 受到了极大的关注[5]。$La(Fe, Si)_{13}$基合金的居里温

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度远低于室温范围, 常用氢化处理的方法提高其居里温度[6-8]。吸氢后的材料仍保持较大的磁热效应, 但是吸氢过程易达到氢饱和, 使其居里温度超过室温范围。加入反铁磁性Mn部分取代Fe可在饱和吸氢后获得室温范围的氢化物, 但是使材料的磁热性能降低[9-11]。吸氢温度和压力等参数对材料的磁热性能有比较明显的影响, 诸多研究集中在吸氢过程对材料磁性能的影响[12, 13]。研究发现, 可控制吸氢后材料的放氢控制氢的吸入量[14-16]。氢原子对居里温度影响显著, 但对最大磁熵变的影响很小。因此, 调控氢含量是获得室温大磁热效应材料的好方法之一[3, 17]。吸氢量的控制成为获得室温磁制冷材料的关键问题之一。

用Pr部分取代La能提高材料的最大磁熵变, 进行氢化处理制备大磁热效应材料也有助于降低材料的磁滞[15, 18-20]。添加微量的B或C等元素有助于缩短材料的退火时间[17, 21], 但过量添加会形成杂相及减弱一级相变, 降低合金的磁热性能[22, 23]。加入微量的B和C等元素有助于减少合金的磁热滞, 促进磁热主相形成, 提高制备效率[24]。本文使用工业纯度原材料制备$La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}B_{0.2}$合金, 先退火吸氢再进行放氢控制, 研究吸氢压力对材料的放氢过程及其磁热效应影响。

1 实验方法

1.1 合金的制备

使用工业纯度La-Fe合金锭、B-Fe合金粉末和Pr锭, 其中La占69.11%、B占29.3%。Fe、Si为块状原料, 纯度为99%以上。样品的名义成分为$La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}B_{0.2}$, 用中频感应熔炼并浇铸成方形板锭。板锭重量为6 kg, 厚度为15 mm。在板锭横断面中部取样退火。将样品放入退火炉内, 先抽真空后充氩气, 在1473 K退火16和30 h后自然冷却到室温。

1.2 吸氢处理

将退火合金破碎后放入真空氢化炉内吸氢, 吸氢温度为553 K, 时间为5 h。吸氢结束后保持氢压自然冷却到室温, 得到$La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}B_{0.2}H_x$氢化物。实验所用吸氢压力分别为0.13 MPa和0.2 MPa。

1.3 放氢处理

将相同重量氢化物放入放氢炉内, 先抽真空, 再充入高纯氩气, 然后升温到473 K放氢处理75-240 min, 得到放氢处理的氢化物。

1.4 性能测试

用Philips PW1830型X射线粉末衍射仪(XRD, Cu$K\alpha$) 分析退火样品的物相。用美LakeShore 7407振动样品磁强计(VSM) 测定样品的M-T和M-B曲线。测量M-T曲线的磁场为0.05 T, 测量M-B曲线的磁场范围为0-1.5 T, 磁场步长为0.05 T。由M-T曲线确定材料的T_C(dM/dT-T曲线中极值点对应的温度即为T_C)。在T_C附近测数条等温磁化曲线M-B, 样品的等温磁熵变为

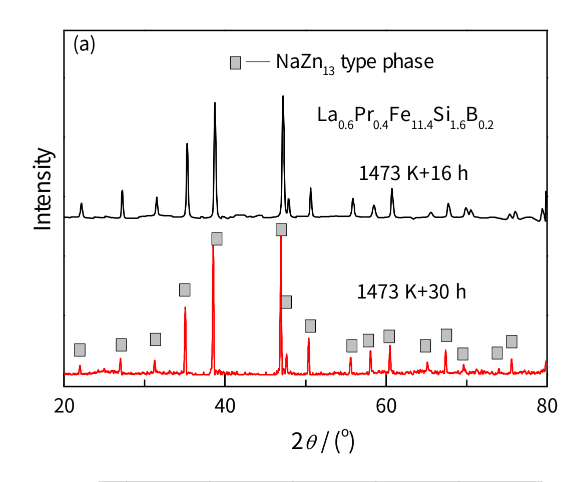
$$\Delta S_m = -\sum_i \frac{M_i - M_{i+1}}{T_i - T_{i+1}} \Delta B_i \quad (1)$$

式中M_i和M_{i+1}分别是磁场为B_i、温度为T_i和T_{i+1}时的磁化强度。

最大磁熵变反应材料的磁热性能, 相对制冷能力RCP(relative cooling power)能更准确的反应材料的磁制冷能力, RCP即最大磁熵变与磁熵变随温度变化曲线的半峰宽温度的乘积[25]。因此, 本文计算样品的相对制冷能力RCP。

2 结果和讨论

图1给出了1473 K退火16和30 h样品的XRD图谱, 图中没有α-Fe和富镧相衍射峰, 只有$NaZn_{13}$型相析出衍射峰。这表明, 合金中形成了大量的磁热



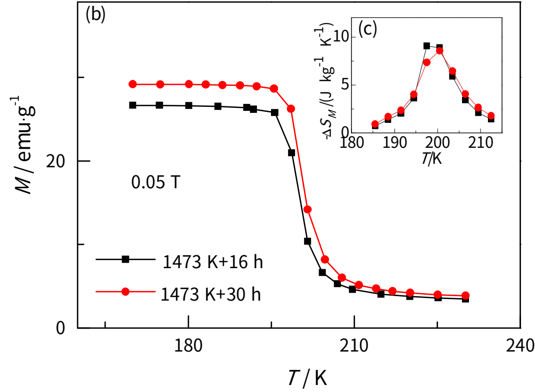


图1 在1473 K分别退火16和30 h样品的XRD图谱、M-T曲线和$\triangle S_M$-T曲线

Fig.1 XRD patterns (a), M-T (b) and $\triangle S_M$-T (insert drawing (c)) of alloys annealed at 1473 K for 16 and 30 h

主相。延长退火时间有助于形成单相磁热相组织且提高磁热主相成分均匀性, 但是退火时间过长使合金最大磁熵变降低和T_C提高[26]。在0.05 T磁场中测试退火样品的升温M-T曲线(如图1b), 对曲线求偏导数由极值点确定16和30 h退火样品的T_C分别为198.7和201.7 K。这个结果表明, 退火时间延长使该成分合金的T_C提高。测量了16和30 h退火样品在T_C附近不同温度等温磁化的M-B曲线, 并使用公式(1)得到退火样品的磁熵变随温度变化曲线(如图1b中插图(c)。在0−1.5 T磁场下, 16和30 h退火样品的最大磁熵变数值分别为9.1和8.6 J/kg·K。使用退火程度更均匀的30 h退火样品进行磁热性能分析, 研究了吸氢压力、放氢时间和放氢温度对氢化物居里温度和磁热效应的影响。

图2给出了退火和吸氢样品的热磁曲线M-T。由图2可知, 退火样品的T_C为201.7 K, 氢化后的样品T_C大幅提高, 超过室温范围。在0.13和0.2 MPa吸氢处理后, 样品的T_C分别提高到320和321 K。吸氢压力不同, 所得氢化物的T_C也不相同, 而且掺杂微量B元素的La(Fe, Si)$_{13}$系合金, 吸氢材料T_C的变化仍符合吸氢压力越大其居里温度越高的规律[3]。

图3给出了吸氢前后$La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}B_{0.2}$合金在$T_C$附近不同温度等温磁化曲线M-B和使用公式(1)得出的磁熵变随温度变化曲线ΔS_M-T。图3a, b, c分别给出了退火样品、0.2 MPa吸氢和0.13 MPa吸氢样品在0−1.5 T磁场下的M-B曲线。由图3d中的ΔS_M-T曲线可知, 退火样品、0.2 MPa吸氢和0.13 MPa吸氢样品在0-1.5 T磁场下的最大磁熵变分别为8.6、8.0和7.9 J/kg· K, 相对制冷能力RCP分别为98、88和88 J/kg。由此可见, 吸氢后$La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}B_{0.2}$样品的磁熵和RCP有所降低, 但是仍保持较大的数值。

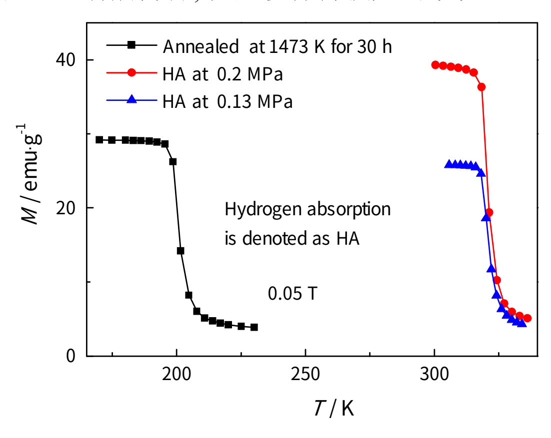
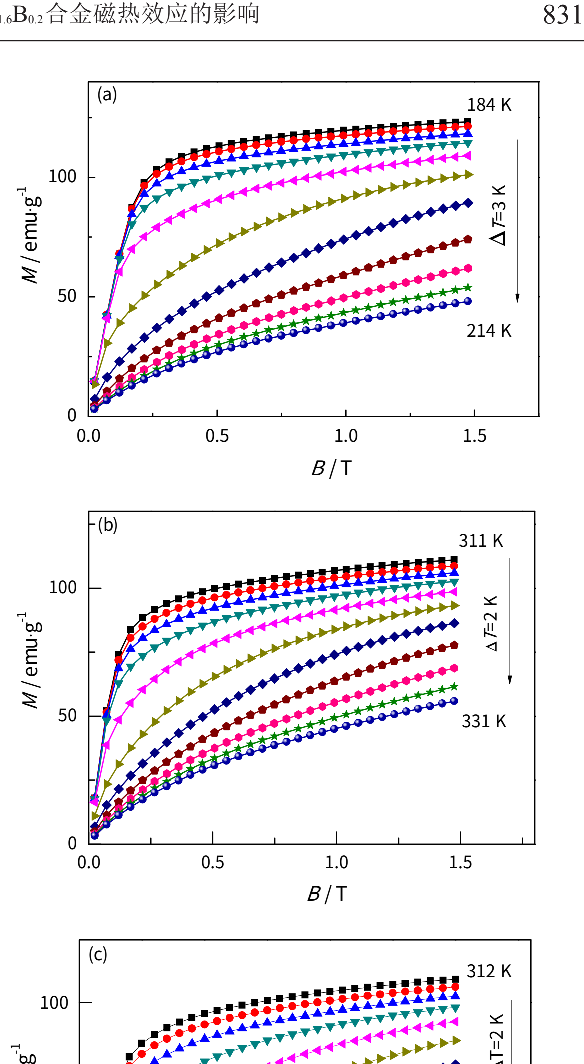
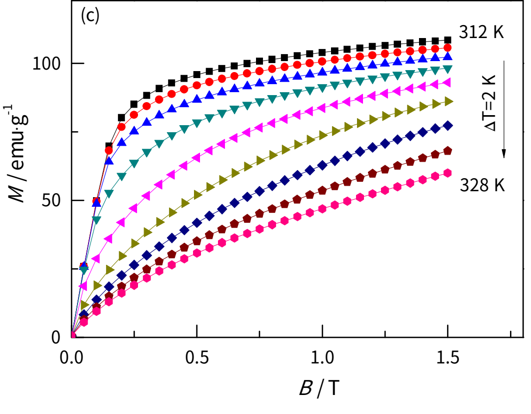


图2　退火及其在0.13和0.2 MPa下吸氢5 h样品的M-T曲线

Fig.2 M-T curves of sample annealed at 1473 K for 30 h and hydrides hydrogenated at 0.13 and 0.2 MPa for 5 h





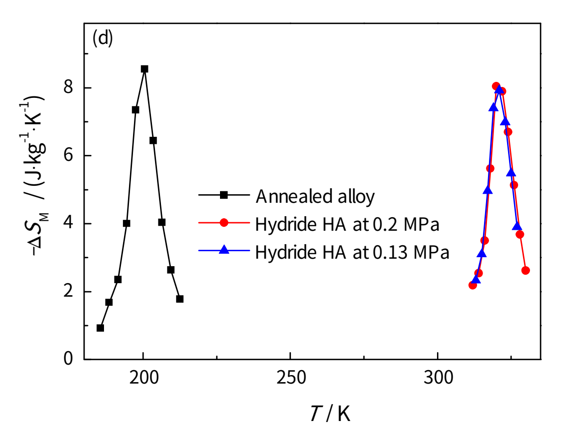
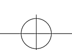


图3　在1473 K退火30 h样品、0.2 MPa和0.13 MPa吸氢样品的*M-B*曲线及其ΔS_M-*T*曲线

Fig.3 *M-B* curves of alloys annealed at 1473 K for 30 h (a), hydrogenated for 5 h at 0.2 MPa (b) and 0.13 MPa (c) along with their ΔS_M-*T* curves (d)



控制放氢时间, 降低氢化物的氢含量, 可将氢化物 T_C降低到室温范围。使用不同吸氢工艺得到的氢化物, 在473 K放氢时氢化物 T_C与放氢时间的关系, 如图4所示。在实验时间范围内, 放氢到一定时间后0.2 MPa吸氢样品的 T_C保持恒定, 而0.13 MPa吸氢样品随放氢时间增加, T_C持续降低。在两种吸氢压力下所得氢化物都有放氢时间越长 T_C降低越缓慢的类似趋势。其原因是, 放氢是在密闭的放氢炉内进行, 放出的氢气和氢化物内的氢原子逐渐达到平衡状态。

对于吸氢压力高的样品, 放氢180 min时 T_c降低到304 K, 放氢时间再延长其 T_C很难进一步降低。对于吸氢压力低的样品, 放氢75 min时 T_C降低到300 K以下, 放氢时间增加到90 min则 T_C降低到295 K。当放氢时间达到105 min时 T_C又进一步降低到294 K, 但是放氢速度明显趋缓。对于相同的放氢温度, 吸氢压力高的样品其放氢速度更低。因此, 吸氢压力高的样品放氢更困难, 稳定性也更高。考虑居里温度的影响, 居里温度高的氢化物放氢速度更低。由于氢化物的居里温度和氢含量密切相关, 吸氢压力高的样品其高稳定性源于更高的氢含量。

放氢处理能降低材料的 T_C, 也影响材料磁热性能。图5给出了放氢样品在 T_C附近不同温度等温磁化曲线M-B和磁熵变随温度变化曲线△S_M-T。图5(a, b, c)分别给出了0.2 MPa吸氢样品经180 min放氢、0.13 MPa吸氢样品经75 min和105 min放氢所得样品的M-B曲线。由图5d中的△S_M-T曲线可见, 在0-1.5 T磁场下0.2 MPa吸氢样品经180 min放氢、0.13 MPa吸氢样品经75 min和105 min放氢所得样品的最大磁熵变分别为6.5、6.8和6.8 J/kg•K, 相对

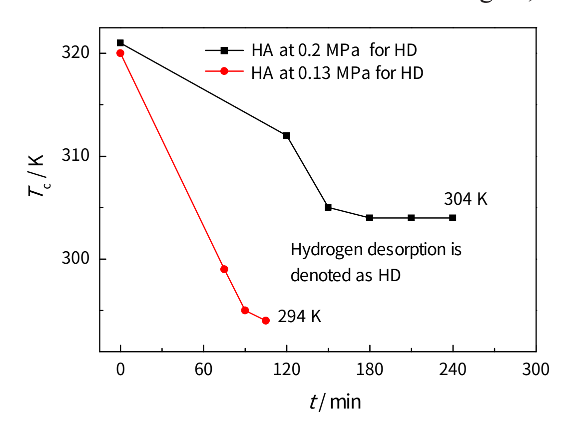


图4 吸氢压力为0.13和0.2 MPa样品放氢处理的 T_C与放氢时间的关系

Fig.4 Relation between T_C and HD times for hydrides samples obtained at 0.13 and 0.2 MPa hydrogen pressures

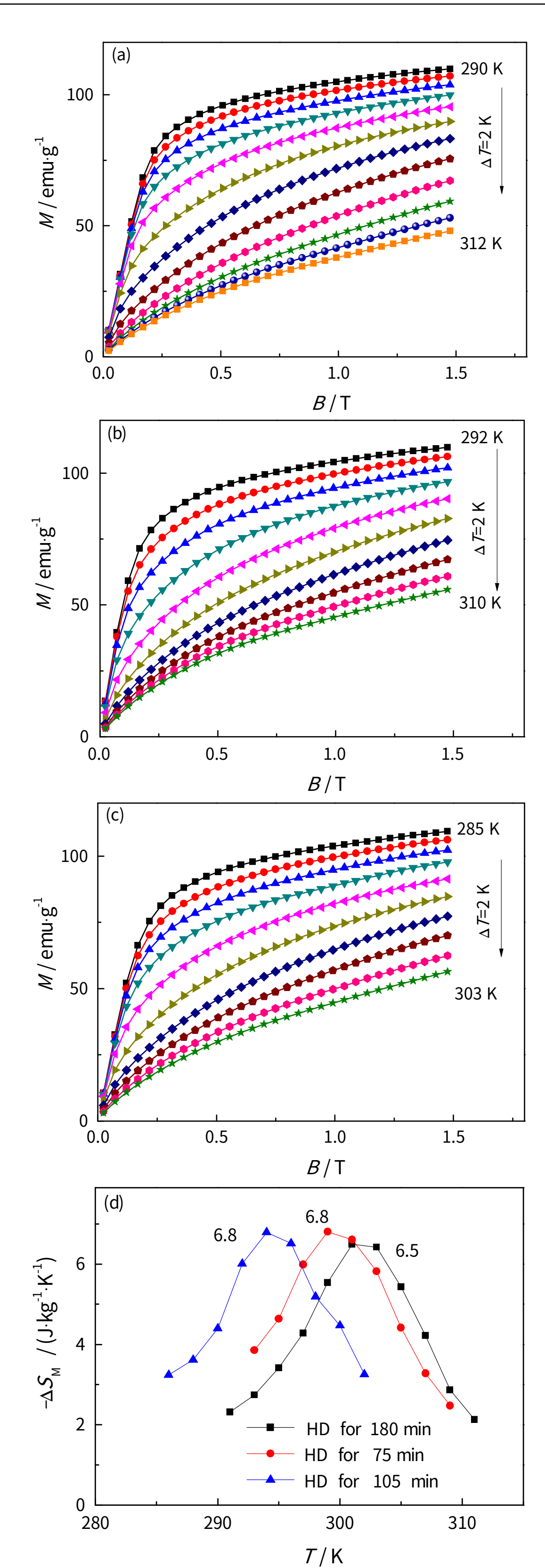


图5 在473 K放氢在0.2 MPa吸氢再放氢180 min、在0.13 MPa吸氢再放氢75 min和在0.13 MPa吸氢再放氢105 min样品的 *M-B* 曲线及其△S_M-T曲线

Fig.5 Hydrogenation desorption *M-B* curves of samples dehydriding at 473 K then hydrogenating and dehydrogenating by HA at 0.2 MPa for 180 min (a), by HA at 0.2 MPa for 75 min (b) and by HA at 0.13 MPa for 105 min (c) and their △S_M-T curves (d)

制冷能力RCP分别为91、102和102 J/kg。需要指出的是, 0.13 MPa吸氢样品经75 min放氢处理样品RCP为估算数值, 因为其$\triangle S_M$-T曲线测量范围未包含整个半峰宽。该值是依据曲线变化趋势延长后得出, 与实际值有一定的差别, 只能用以判断变化趋势。由以上分析可知, 放氢样品的最大磁熵变比吸氢样品低, 但是放氢样品的相对制冷能力RCP值比吸氢样品的高, 放氢样品仍具有较高的室温磁制冷能力。

3 结 论

1. $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}B_{0.2}$合金在放氢过程中释放的氢气与金属内的氢形成平衡, 放氢超过一定时间后T_C趋于恒定, 其恒定温度与氢化物中氢含量相关。吸氢样品在473 K进行放氢处理后最大磁熵变降低, 相对制冷能力RCP值提高。

2. 吸氢压力对放氢过程有显著的影响, 吸氢压力越大则氢越不易释放, 所得氢化物的稳定性越好。吸氢压力高, 氢化物的高稳定性, 源于更高的氢含量。

3. 使用工业原料、吸氢和放氢处理可制备出具有室温大磁热效应的氢化物磁制冷材料。对0.13 MPa吸氢样品在473 K放氢处理, 氢化物的T_C为294 K, 在0−1.5 T磁场下该氢化物的最大磁熵变为6.8 J/kg·K, RCP为102 J/kg。

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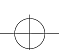
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